# We are IntechOpen, the world's leading publisher of Open Access books Built by scientists, for scientists

**4,800**
Open access books available

**122,000**
International authors and editors

**135M**
Downloads

Our authors are among the

**154**
Countries delivered to

**TOP 1%**
most cited scientists

**12.2%**
Contributors from top 500 universities


WEB OF SCIENCE™

Selection of our books indexed in the Book Citation Index in Web of Science™ Core Collection (BKCI)

## Interested in publishing with us?
## Contact book.department@intechopen.com

Numbers displayed above are based on latest data collected.
For more information visit www.intechopen.com

Chapter 1

# Excitonic Crystal and Perfect Semiconductors for Optoelectronics

Sergei L. Pyshkin

Additional information is available at the end of the chapter

http://dx.doi.org/10.5772/60431

**Abstract**

This chapter demonstrates the growth of perfect and contamination-free gallium phosphide (GaP) crystals and discusses the influence of crystallization conditions on their quality and properties. The long-term ordered and therefore close to ideal crystals replicates the behavior of the best nanoparticles exhibiting pronounced quantum confinement effect. These perfect crystals are useful for application in top-quality optoelectronic devices as well as they are a new object for the development of fundamentals of solid state physics.

Since samples of gallium phosphide doped by nitrogen (GaP:N) were originally prepared by the author in the 1960s, followed by the introduction of the excitonic crystal concept in the 1970s, the best methods of bulk, film and nanoparticle crystal growth have been elaborated. The results of semi centennial evolution of GaP:N properties are compiled here. Novel and useful properties of perfect GaP including its stimulated emission, very bright and broadband luminescence at room temperature were observed. These results provide a new approach to selection and preparation of perfect materials for optoelectronics and a unique opportunity to realize a new form of solid-state host — the excitonic crystal as high intensity light source with expected low threshold for the generation of non-linear optical phenomena.

Using the example of GaP here is proposed as a cheap, resource-saving and impactful way to develop optoelectronics through a special transformation of an ordinary semiconductor into the base material for various device structures.

**Keywords:** GaP, long-term ordering, excitonic crystal, perfect semiconductors for optoelectronics

## 1. Introduction

Single crystals of semiconductors grown under laboratory conditions naturally contain a varied assortment of defects such as displaced host and impurity atoms, vacancies, dislocations, and impurity clusters. These defects result from the relatively rapid growth conditions and inevitably lead to the deterioration of mechanical, electric, and optical properties of the material, and therefore to degradation in the performance of the associated devices. Note, the deterioration of optical properties of any luminescent material for application in optoelectronics may appear in the complete absence of light emission in the spectral region, where the perfect material gives an excellent luminescence, in too narrow emissive band, in a very weak light emission, in impossibility to control its shape and brightness, as well as in fast degradation of a device prepared on the base of this material. In order to partly overcome the noted preceding difficulties, industry uses expensive but only palliative decisions such as limitless extension of the list of materials for the device making or small improvement of technologies for growth and preparation of electronic materials. Huge material, time and mental resources already have spent and will be spent further in our efforts to support or improve achieved parameters and reliability of electronic devices. Therefore, finding of alternative drastic methods for device making is one of the main priorities of electronic industry development. This paper describes the experience of the author in this field.

The pure and doped GaP crystals discussed herein were prepared about 50 years ago [1]. Throughout the intervening decades they have been periodically re-evaluated in order to investigate the marked changes over time in their electro- and photoluminescence, photoconductivity, behavior of bound excitons characteristic for doped GaP, nonlinear optics, and other phenomena. Accordingly, it was of interest also to monitor the change in crystal quality over the course of several decades while the investigated crystals are held under ambient conditions.

Over time, as it is confirmed by the author during 50 years of the relevant experiments, that driving forces such as diffusion along concentration gradients, strain relaxation associated with clustering, and minimization of the free energy associated with properly directed chemical bonds between host atoms result in an ordered redistribution of impurities and host atoms in a crystal. In the particular case of GaP and some other chemical compounds, having in their compositions highly volatile components, any attempt to accelerate these processes through annealing at increased temperatures cannot be successful because high-temperature processing results in thermal decomposition (in GaP — due to P desorption) instead of improved crystal quality. Therefore, successful thermal processing of these compounds can only take place at temperatures below the sublimation temperatures of their volatile constituents, requiring a longer annealing time. For instance, evaluated in the framework of the Ising model, the characteristic time of the substitution reaction during N diffusion along P sites in GaP:N crystals at room temperature constitutes 15–20 years [2]. Hence, the observations of luminescence and some other phenomena in the crystals made in the 1960s–1970s and in the 1980s–1990s were then compared with the results obtained in 2005–2014 under similar experimental conditions.

The long-term ordering of doped GaP and other semiconductors has been observed as an important accompanying process, which can only be studied using the same unique set of samples and the interest to observe them over decade time scales. More specifically, the optical and mechanical properties of single crystalline GaP, and some other semiconductors also grown in the 1960s, have been analyzed. Comparison of the properties of the same crystals has been performed in the 1960s, 1970s, 1980s, and 1990s [1, 3-17] along with those of newly made GaP nanocrystals [18-20] and freshly prepared bulk single crystals [21-24]. Jointly with the references [25-27], this review provides a generalization of the results on long-term observation of luminescence, absorption, Raman light scattering, and microhardness of the bulk single crystals in comparison with the same properties of the top quality GaP nanocrystals. It is shown that the combination of these characterization techniques elucidates the evolution of these crystals over the course of many years, the ordered state brought about by prolonged room-temperature thermal annealing, and the interesting optical properties that accompany such ordering. It is demonstrated that long-term natural stimuli that improve the perfection of crystals prevail over other processes and can lead to novel heterogeneous device systems and new semiconductor devices with high temporal stability.

Additionally, it is worth noting, that semiconductor nanoparticles for optoelectronic applications also were synthesized mainly to avoid limitations inherent to freshly grown bulk semiconductors with a wide range of different defects. For instance, different defects of high concentration in freshly prepared GaP single crystals completely suppress any luminescence at room temperature due to the negligible free path for non-equilibrium electron-hole pairs between the defects and their non-radiative recombination, while the quantum theory predicts their free movement in the field of an ideal crystal lattice. However, the long-term ordered and therefore close to ideal crystals even at 300K demonstrate bright luminescence and stimulated emission equivalent to the best nanoparticles. These perfect crystals, due to their unique mechanical and optical properties, are useful for application in high-quality optoelectronic devices as well as they are a new object for the development of fundamentals of solid state physics, nanotechnology, and crystal growth.

Also noted is the application of GaP/polymers nanocomposites in device structures for accumulation, conversion and transport of light energy that has only recently received attention while bulk and thin GaP films have been successfully commercialized for many years. Therefore, for completeness, during the recent years, since 2005, the author and colleagues continued their efforts on the preparation of GaP nanoparticles in order to improve their quality and to apply their composites with appropriate polymers for advanced light emissive structures [18-20, 28-32].

In preparing this review, the author did not intent to evaluate the works on GaP of the other authors, but their works are cited and used here when it is necessary for explanation and interpretation of new phenomena observed during long-term ordering of impurities and host atoms in the crystal lattice. Elaborating optimal methods of preparation of GaP bulk crystals, nanoparticles and their light emissive composites with compatible polymers, we use our own experience and literature data [33-42]. The main goal of these 50 year efforts and this review are the observation and description of very interesting results of the long-term evolution of GaP properties and the relevant idea to propose for many years ahead an alternative and resource-saving way for the development of electronics, as well as to propose and justify the

excitonic crystal [26, 27] as a new optical media for the future optoelectronic devices used in optical data processing, storage, and transmission as well as for the generation of non-linear optical effects at rather modest thresholds for nonlinearities. Interesting and very useful for application results of long-term evolution of GaP properties as well as the unique collection of tested and stored for years pure and doped perfect GaP crystals are demonstrated and proposed to academic researchers, engineers, and managers of electronic industry for intensification of collaboration in patent activity, reorganization of the material and device making processes, reduction in price, improvement of parameters, and reliability of devices.

Perfect GaP single crystals, excitonic crystal on the base of the GaP crystal doped by nitrogen (GaP:N), as well as understanding of properties and available application of these new objects coming these days into science and industry are the result of intense many years work of headed by the author groups of top specialists on crystal growth, investigation of their properties, and application in optoelectronics in Russia, Moldova, the USA, and Italy. This activity was stimulated and followed by the natural processes and phenomena elapsed with time in the crystals.

According to the chosen plan of presentation, this review is divided into the next sections:

**1.** Introduction

**2.** Properties of GaP

**3.** Growth Technology for Perfect GaP Bulk and Nano-Crystals

**4.** Optical Properties of Perfect, Long-term Ordered GaP:N Crystals

**5.** Comparison of Properties of GaP Nanocrystals and GaP Perfect Bulk Single Crystals

**6.** Excitonic Crystal and Its Importance in Optoelectronics

**7.** Already Discovered and Possible Nonlinear Optical Phenomena in GaP

**8.** Conclusions

**9.** Acknowledgments

**10.** References

## 2. Properties of GaP

GaP crystallizes in zinc blende structure, where Ga and P atoms create two interpenetrating face-centered lattices spaced ¼ of the (111) cube diagonal apart.

Brillouin zone of GaP and other III-V compounds represent the truncated octahedron (Figure 1) having the next high symmetry points:

$\Gamma - \overline{K} = (000)$ — center of Brillouin zone

$\Delta$ — along the (100) axis inside the zone

http://dx.doi.org/10.5772/60431

X — (100) Brillouin zone edge

∑ — along the (110) axes inside the zone

K — (110) Brillouin zone edge

Λ — along the (111) axes inside the zone

L — (111) Brillouin zone edge

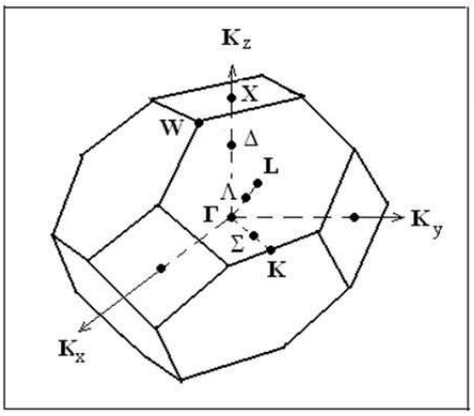


**Figure 1.** Brillouin zone of gallium phosphide.

A concrete band structure for each III-V representative in the limits of common for them Brillouin zone depends on the type of symmetry of the wave functions of valence electrons of the atoms, creating the compound. The most reliable data on GaP band structure were obtained from the experiments on light absorption and reflection as well as using the spectral distribution of photoconductivity in the region of intrinsic absorption.

According to W. Paul's empirical rule [36], the energy gaps equally depend on the pressure for the relevant electron states. Using this rule and experiments on dependence of electron transitions on pressure, the authors of Ref. [37] have proposed the band structure of GaP presented in Figure 2.

Experimental data confirm the details of the GaP band structure. So, the absolute minimum of the conductance band (the X-point) presented in Figure 1 lays at the edge of the Brillouin zone in the (100) direction, while the valence band maximum (the Γ-point) position is the center of the zone. The absolute minimum value of the forbidden gap (Figure 2) corresponds to the indirect optical transition $\Gamma_{15}^{v} \rightarrow X_1^{c}$; this value depends on the temperature changing between 2.354 eV at 4.2K (liquid helium) and 2.328 at 77K (liquid nitrogen) until 2.248 eV at 300K (room temperature) [37]. Minimum gap for direct optical transition $\Gamma_{15}^{v} \rightarrow \Gamma_1^{c}$ at 300K is equal to 2.78eV [37]. The valence band, taking into account its spin-orbit splitting, consists of two confluent bands and another one shifted downward. The other details of GaP band structure are shown in Figure 2.

According to the quantum selection rules for optical transitions, the lattice phonons do not participate in the direct transitions, while in the indirect transition lattice phonons participate,

the type and energy of which are determined in Ref. [38] together with the low- and high-frequency dielectric constants, 10.182 and 8.457, respectively. The data on GaP phonon spectrum are widely used at interpretation of its light emissive and absorption spectra. In indirect optical transitions [38, 40] participate transversal and longitudinal acoustic and optic phonons with energies 12.8 (TA), 31.3 (LA), 46.5 (LO), and 50.0 meV (TO). Note, at low temperatures, when the thermal energy, kT, is less than the respective energies of the free and bound exciton creation (10 and 21 meV, respectively, for free and N bound excitons [4, 7]), the indirect optical transitions occur mainly through the excitonic states.

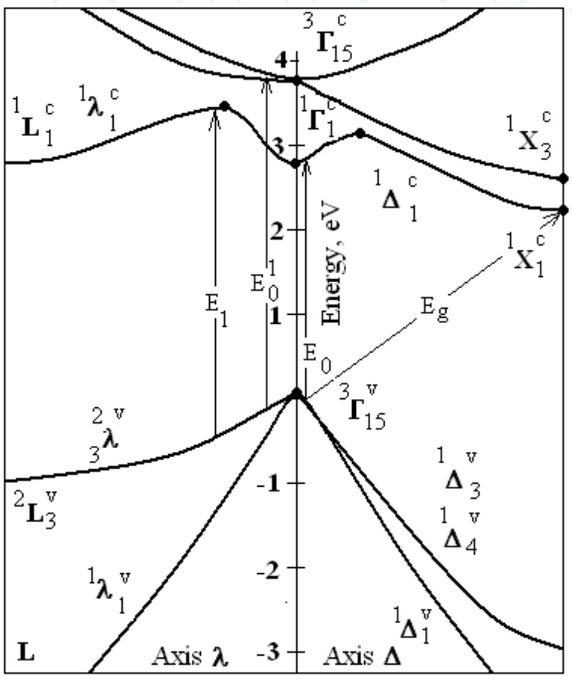


**Figure 2.** Band structure of gallium phosphide.

## 3. Growth Technology for Perfect GaP Bulk and Nano-Crystals

Single crystals of gallium phosphide, in principle, can be obtained in several ways [1, 3, 7]. The method for obtaining gallium phosphide from solution-melt, chosen by us, has several significant advantages:

1. A significant temperature reduction of the process and the presence of large amounts of solvent dramatically reduce crystal pollution by material of the container.
2. The light sources creating on their basis have high efficiency.
3. Due to specifics of the method, gallium phosphide at the appropriate level of the experiment can be obtained in the form of the relatively large lamellar crystals of a definite crystallographic orientation. Note, lamellar crystals are the most convenient and economical material in the manufacture of many semiconductor devices.

http://dx.doi.org/10.5772/60431

Consider the peculiarities of growth of lamellar crystals of gallium phosphide with the set-up properties, formed under uniform cooling of the P solution in Ga. The influence of the following factors has been investigated: 1) quantity and chemical nature of impurities; 2) geometric shape of the container and conditions of heat rejection; 3) accuracy of the temperature control; 4) cooling rate and the law of temperature change in time.

The aim of this work was to elucidate the mechanism of crystallization of lamellar GaP crystals and experimental confirmation stated earlier assumptions about the nature of this process.

I. The solution-melt method of GaP growth is described in detail in Refs.[1, 3, 7]. So we focus here only on the characteristics for this study associated of the crystal growth.

Synthesis, alloying, and crystallization were combined in a single cycle. Experiments on the establishment of the influence of impurities on the growth of GaP crystals was performed using Ga000 and phosphorus B5, industrially prepared in former USSR, the highest purity produced at that time (1960). When the growth process was thoroughly investigated, the growth of perfect crystals has been conducted in a sealed and drained simple container from optical quartz that was flushed with spectral pure argon (Figure 3a). Container 1 was introduced into the programmable furnace with rod 2 fixed on the vibrator to agitate the mixture of Ga, P, and any chosen dopant, to facilitate chemical reaction between components, and to avoid a possible explosion of the container in dangerous temperature points of the process of mass crystallization (Figure 3a). However, for investigation of the growth process some other containers were used. For instance, the container having a good thermal isolation of the walls and a Cu metal rod on its bottom was used to create the center of crystallization for needle-like crystals (Figure 3b). The container, comprising the set of necessary growth components 4, thermoisolating layer of $Al_2O_3$ 6, Ga etalon 7, and thermocouples in the critical places 5, 8, has been used for the investigation of thermal processes during the crystal growth (Figure 3c). At last, the upside-down rotatory container with the thin quartz net 9 was used to see and investigate the crystal forms at different growth regimes (Figure 3d).

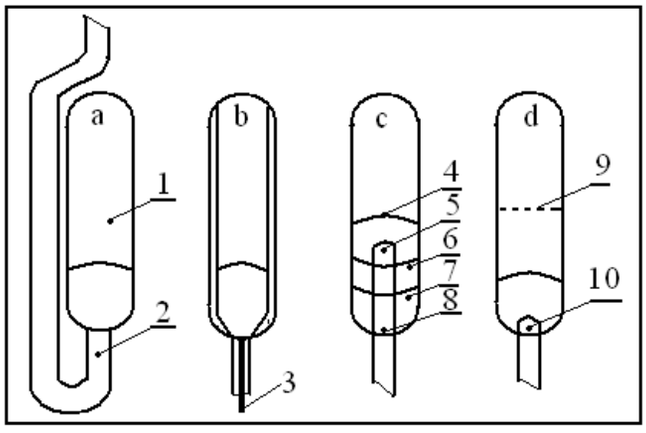


**Figure 3.** The containers for growth of perfect GaP crystals and investigation of the growth process. **a**, **b**, **c**, **d**. Types of containers. 1. Silica ampule. 2. Silica inlet rod, fixing the ampule to the vibrator. 3. Cu metal rod. 4. Container for investigation of thermal processes. Points 5, 8, 10 — locations of thermocouples. 6. Thermoisolating $Al_2O_3$ layer. 7. Ga etalon. 9. Silica net.

The impact of the temperature control accuracy was investigated at the facility, which allows to reproduce with controlled accuracy the necessary law of the temperature change in the growth container [1, 3]. Permissible fluctuation of temperature can be set within ± 0.5 ± 10° C interval. In order to study the form and quality of growing crystals, the crystallization process could be interrupted at any temperature below the point of liquidus. This interruption was achieved with the help of a special designed growth container (Figure 3d) and its programmable heating furnace, which allow to stop the change of temperature of the solution-melt, to identify and examine the crystals grown to this time (see details in [1, 3]).

Let us now describe and explain the peculiarities of temperature regime during the growth of lamellar perfect GaP single crystals from approximately 10 $cm^3$ of 5 at.% P – Ga melt solution (Figure 4). The smoothly heated slightly over 400°C solution must be kept for around 2 hours at this temperature for safe, non-dangerous explosion transformation of red phosphorus into its white modification. Then the heating process may be smoothly prolonged until a temperature of approximately 1200°C that increases the liquidus point for 5% P solution in Ga (1123°C) and creates good conditions for Ga-P reactions. After 1–3 hrs. soaking interval start to gradually cool the solution with a velocity of around 30°C/hrs. until 600–700°C and shutoff of the furnace. For perfect quality of the growing crystals during this 12–15 hrs. cooling of the solution, it is extremely important to support very fine, ±0.5°C temperature control possible with the specially elaborated heating and temperature control installation [3].

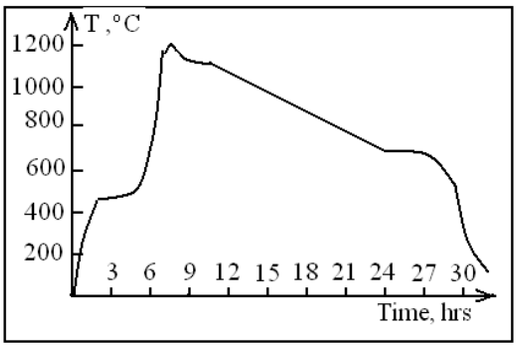


**Figure 4.** Programmable temperature changes in growth container.

With the introduction into the Ga solvent of various impurities, the choice of which was determined by practically important properties of the obtained crystals, at the same time the effects of contaminants on the nature of solidification have been investigated. The following impurities were introduced one by one in the solvent: Cu, Zn, Cd, In, Si, Ge, Sn, S, Se, Te, Ni, Cr, Fe, Co, Sm, La, Gd, and $Sm_2O_3$.

Typical features of the doped GaP crystals (size, color, polarity, lamellar structure, twinning, the dislocation structure, and others) were compared with similarly grown but undoped crystals.

It was found that the properties of the crystals depend on the chemical nature as well as on the quantity of the selected impurities. Their small admixtures did not significantly change the form of the crystals, while significant change of the crystallization environment composition

created changes in forms of growth. For instance, the introduction into the solution of large quantities of Sn, the element of another valence compared with Ga, led to the emergence of the crystals having octahedral isometric forms. Isometric forms with simultaneous reduction of the sizes of crystals occurred with the introduction of solvent refractory impurities — samarium oxide ($Sm_2O_3$), solid units of which, apparently, were the centers of crystallization. Introduction into the solution of significant quantities of In, the chemical analogue of Ga, only slightly influenced on the morphology of the crystals, changing the lattice parameter, indicating the formation of 0.01 at. % In-GaP solid solution.

It was established that an increase in concentration of Zn and Gd in the Ga-P solution leads to the increase in the concentration of carriers (holes), reducing the size of crystals and their chemical resistance with a simultaneous increase in microhardness on the plane (111). At the introduction of S (1 at. % and more) the forms of the crystals varied from lamellar to volumetric. By increasing the concentration of tellurium in solution from 0,007 to 0.02 at. % the lattice constant varied from 5.4511 to 5.4524Å. At small quantities of impurities Zn and Te in GaP, until about $10^{19}$ $cm^{-3}$, a direct proportional relationship between the amount of impurities added to the solution and the concentration of charge carriers in the crystals is observed. Doping of the Ga-P solution by small quantities of rare earths and elements of the Fe group did not impact significantly on the forms of crystals, however, led to a significant change in the electrical and luminescent properties of GaP crystals. It is interesting to note that the density of etching pits on the plane (111) of doped crystals sharply increased in comparison with undoped ones.

III. The following factors influenced on the morphology of GaP crystals grown from the Ga-P solution of a certain concentration in conditions of the mass crystallization: the degree of supersaturation, which depends on the temperature of the solution and its first time derivative, the conditions of the heat crystallization removal and the accuracy of the temperature control in the solution.

Changing conditions of crystallization, mainly the rate of cooling of the melt, significantly affects the morphology of crystals. So, increasing the cooling rate reduced the size of the crystals, but the dislocation density was not changed and was primarily the determined concentration and chemical nature of impurities. The number of crystals having isometric forms increased with the decreasing cooling rate at simultaneous improvement of quality of the crystal surface. Uneven removal of heat from walls of the container has led to the formation of up to 30 mm crystal needles, elongated in the direction of the heat removal.

Significant impact on the crystal quality provides more accurate temperature control. The crystals obtained with the accuracy of temperature control ±0.5°C had a perfect plane (111), low dislocation density, and dimensions in 2–3 larger than the crystals obtained at the same conditions, but with the accuracy ±5°C or according to the regimes described in the literature. Crystals reached 25 mm in length and had the dislocation density ~ $10^3 cm^{-2}$, which is significantly less than that of the crystals obtained with low accuracy of the temperature control.

IV. In order to clarify the mechanism of crystallization of lamellar GaP crystals, differential record of temperature change between the standard of pure Ga and 5 at.% Ga-P solution near

the point of liquidus as well as interruption of the crystallization process at different temperatures below the point of liquidus were conducted in special containers presented in Figure 3c and 3d (please see details described in Refs.[1, 3]). The record of temperature was conducted in the locations of the Ga standard and the Ga-P solution, interruption of the process was carried out by turning the container with quartz net from the top down. The pattern of temperature change in the solution-melt is presented in Figure 5.

Let us now present an overview of the growth of lamellar GaP crystals basing on the findings of these experiments. Total quantity of the solution-melt in the experiments was 10–12 $cm^3$, 1 $cm^3$ of this solution (5 at.% of P) at a temperature above the line of the liquidus contained $3x10^{21}$ and $6x10^{22}$ of P and Ga atoms, respectively. The first crystals, having the form of dendritic needles with the length of the order of 5 mm and thickness of 0.15 mm, were registered at a temperature of 1107°C at approximately 16°C supercooling. The crystals, found on the net inside the growth container [1] at lower temperatures of the process interrupting, represent thin plates in the form of rhombs, triangles, or hexagons. The twinning on the transverse cross-sections was observed at the study of microsections and cleaved facets. It turned out that the lamellar GaP crystals contain the plane of twinning, parallel to the planes (111).

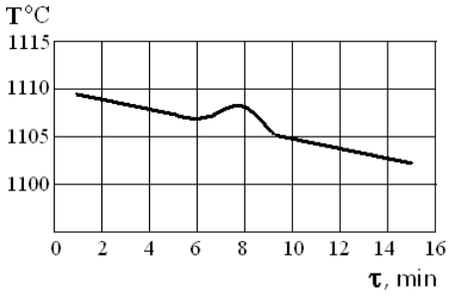


**Figure 5.** Change of temperature in the container when cooling with 30 deg/hour the 5 at.% solution of P in Ga.

The growth process of lamellar crystals can be formally divided into two components: the tangential growth in the plane (111) and layer-by-layer growth in the direction normal to the plane (111). Because the ratio of Ga and P atoms differed significantly from the stoichiometric, it is natural to assume that the process determining the rate of growth is diffusion. According to our estimates, the coefficient of diffusion of phosphorus atoms in Ga at T~1400K is equal $D_p$ ~$3x10^{-3}$ $cm^2sec^{-1}$.

Upon cooling the system to 1107°C degrees, the supercooling of the solution was approximately $1.6x10^{20}$ $cm^{-3}$. Accepting the growth of needle-shaped crystals ends during recalescence time about 2 min (Figure 3), we get the diffusion length $L = (D_p \cdot \tau)^{1/2} = 0.6$ cm, and, further, the dimensions of the crystal in diffusion approximation: needle length 6 mm and thickness 0.56 mm; this value is in a good agreement with the experimental data. With further lowering of the temperature, the crystals acquire lamellar form with mainly developed planes (111) having the greatest reticular density and composed of the same atoms. Note that the removal of heat of crystallization is facilitated by the lamellar form of the crystals.

http://dx.doi.org/10.5772/60431

Thus, accepting the above presented two-stage model of lamellar crystal growth, let us consider the ratio of the contributions of the tangential growth in the plane (111) and layer-by-layer growth in the direction normal to the plane (111). The growth in the tangential direction is limited by diffusion and by the size of the previous layer, that is, it is determined by the initial conditions and the shape and size of the plates, formed during the cooling of the solution-melt 10–20 degrees below the point of liquidus. Since the formation of the initial crystals occurs in a very short time, the growth in the tangential direction is difficult to control, as it is in the case of the dendritic crystal growth. The growth in the direction normal to the plane (111) is sensitive to the fluctuations of the degree of supersaturation, resulting from the thermal motion of atoms and temperature fluctuations. In general, uniformity and perfection of the surface of lamellar GaP crystals the better, the less the time ratio needed for formation a new layer on a flat nucleation center to the time for which will be created the next nucleation center. The latter, obviously, in an extreme extent depends on fluctuations of the degree of supersaturation in different points of the growing plane and at different points in time. With the deterioration of precision temperature control, the number of fluctuations increases and bad crystals grow in the conditions of "entanglement" of the above mentioned characteristic times. Small fluctuations of supersaturation also are probably the cause of twinning planes. Indeed, assuming that the probability of fixation of the twins on the plane (111) is $W = \exp(-n\varepsilon/kT)$, where n is the number of atoms in a flat nucleus and $\varepsilon$ is the energy of packing defect per atom, and knowing the ratio of the number twin planes to normal equals $10^{-5.5}$, we obtain $W = \exp(-n\varepsilon/kt) = 10^{-5.5}$, $k = 1.4 \times 10^{-16}$ erg/degree, T = 1400K, and $n\varepsilon = 1.6$ eV or n = 10, $\varepsilon = 0.16$ eV/atom that under the order of the values is reasonable.

Increase of the accuracy of temperature regulation promotes some reduction in the number of twins and this fact also confirms the notable influence of fluctuations on the twinning.

Thus, deteriorations of quality or shape defects of GaP plates during their growth from Ga – P melt solution are observed in the next cases: 1) at a considerable increase of concentration of impurities in the GaP solution and dependently on the chemical nature of the chosen impurity; 2) at the change of the crystallization conditions, namely, at the sufficient deterioration of the cooling velocity control or in the case of nonuniform heat removal from the container for the crystal growth.

Processes of creation of the dendritic needles and their transformation to platelet crystals take place in a small temperature interval and for a short time, therefore they are hardly controlled, while crystal growth is easily controlled in the direction normal to the plate (111), because it is very sensitive to the external factors such as velocity of the solution cooling and accuracy of the temperature control.

All the above-stated means that only very perfect growth equipment and top quality growth experience will give an opportunity to grow good and high service ability GaP crystals. However, in spite of all precautions and high experience of the specialists, growing the crystals, freshly prepared GaP crystals cannot be successfully applied in electronics due to their low operational data, such as absence of high photosensitivity, bright and broadband luminescence, satisfactory transparency, and mechanical characteristics. Further, it will be shown how to considerably increase the quality and service ability of the freshly prepared GaP crystals.

## 4. Optical Properties of Perfect, Long-term Ordered GaP:N Crystals

It is necessary to note that the very important for optoelectronics long-term ordering and considerable improvement of the semiconductor crystal lattice and accompanying phenomena have been discovered and observed over decade time scales only with the help of the same unique collection of samples. This collection of long-term ordered perfect GaP single crystals gives opportunities to find deep fundamental analogies in properties of the perfect single crystals and nanoparticles as well as to predict and to realize in nanoparticles and perfect bulk crystals new interesting properties and applications.

Investigating the samples grown by the author in the 1960s, it was noted [1, 7], gallium phosphide (GaP) crystals for the first time clear improved their optical and mechanical properties only after 10–12 years since their preparation. It was unusual and interesting in the situation when all non-living matter around us usually deteriorates in time; therefore the author decided to investigate, to understand, and to use in the future this phenomenon. Shortly, the investigation process can be described as following.

Grown about 50 years ago pure and doped GaP crystals throughout the intervening decades have been periodically re-evaluated in order to see and investigate the change over time in their electro- and photoluminescence, photoconductivity, behavior of bound excitons, giving interesting and bright luminescence, nonlinear optical, and other phenomena. Accordingly, it is of interest also to monitor the change in crystal quality over the course of several decades while the crystal is held under ambient conditions.

Figure 6 demonstrates Raman spectra in GaP and GaP:N in 1989–1993 (a) and in 2006 (b, c). Concerning the general differences in the Raman spectra produced by the ordered and disordered forms of the crystals, note in accordance with Refs. [10, 17, 21-24] that the spectrum of the most ordered heavily N doped crystal (spectra 2 in Figure 6b) shows a considerably more intense narrow LO line than the less ordered pure or doped crystals (spectra 3, 4 in Figure 6b). Whereas the distribution and the environment of the P or N anions at a particular site in the unit cell in the ordered crystal are uniform, the great variability in this environment from site to site exists in a disordered or less ordered crystal.

Note that the theory of Raman light scattering in GaP predicts the LO phonon decay into two longitudinal acoustic phonons LA. LA phonons with a frequency LO/2 [41], and 2-phonon processes of 2TO and TO+LO emission also can be observed in perfect crystals [42]. This observation of a multi-phonon process and a decay of LO phonon, having a low intensity, confirm the high quality of the host lattice, uniform impurity distribution, and as a consequence, low noise background in the Raman scattering.

Figure 7 provides the Raman spectra obtained in 2005–2006 from pure and heavily doped GaP at 300K (a) and 80K (b). It can be seen only in the GaP:Bi crystal at 300K that a very narrow LO phonon is slightly shifted (approximately 2 $cm^{-1}$), while the TO and LO peaks maintain their spectral positions at 80K for the pure and doped GaP crystals independently of the type of impurity and its concentration. The LO phonon line is narrower in the doped crystal than in the undoped (pure) one and also is more intense than the TO phonon line. Note that these results are obtained despite the fact that the maximum concentrations of N, Sm, and Bi in these

http://dx.doi.org/10.5772/60431

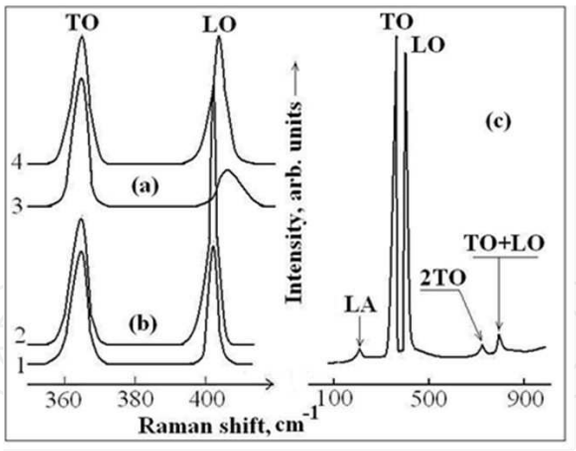


**Figure 6.** Raman spectra in GaP and GaP:N in 1989–1993 (a) and in 2006 (b, c). 1, 4—pure GaP, 2, 3—GaP heavy doped by N. Spectra 3, 4 are taken from Ref. [11] and obtained by one of the authors (SLP) in 1991. A new phenomenon observed in the Raman spectra that has developed in the crystals over 40 years are the peaks denoted by us here as LA, 2TO, and TO+LO (Figure 6c).

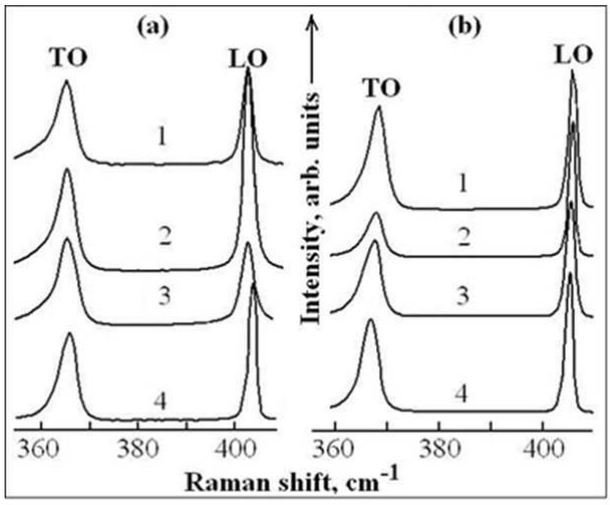


**Figure 7.** Spectra of Raman light scattering of pure and doped GaP at 300K (a) and 80K (b). 1. Pure. 2-4: GaP doped by N, Sm, and Bi, respectively

crystals are close to their limit of solubility (~ $10^{19}$cm$^{-3}$), the masses of impurity atom are very different, (the atomic weight 14, 150, and 208 for N, Sm, and Bi, respectively), and the N and Bi impurities substitute lattice points whereas Sm occupies interstitials.

The position and the line-width of the TO line in the ordered crystals do not depend on type and concentration of impurity nor on temperature. The temperature-independent TO line-width in the aged crystals implies that the impurities do not perturb the order of the lattice, which is possible only for a very uniform environment.

It is known that the broadening and frequency shift of the phonon lines are due to anharmonicity of the lattice vibrations and disorder in the crystal. Note that the TO line-shapes in the crystals again measured after 17–19 years are more close to Lorentzian than in [41] and LO

lines are narrower in the crystals with big impurity concentrations. This most likely means that the anharmonicity of the lattice vibrations in the presence of ordered impurities is less than that in the pure unordered crystals. An increase in temperature only slightly distorts the TO line-shape in these crystals implying that the anharmonicity also is weak. Considering these results, it is assumed that the anharmonicity is larger in perfect undoped crystals than in doped crystals with periodically disposed impurities. Thus, it has been observed that in long-term ordered GaP crystals different impurities presented there at high concentrations do not distort crystal lattice, lead to narrowing and increase of longitudinal optical mode LO, and do not change the symmetrical form and positions of the TO line.

After 40 years since their fabrication the impurities in these doped GaP crystals create a superlattice with a period that depends on their concentration. Absence of luminescence from bound pair excitons (which need for their creation considerably less NN spacing than it is possible at the N concentration in our GaP:N crystals) as well as the spectral position of the narrow zero phonon line A shifting along the luminescent spectrum dependently on the N impurity concentration in exact correlation with the relevant theoretical ratio (see [40] and Figure 8a) only clearly show that in the 25–40 years aged GaP:N crystals the impurity atoms are located with the equal $r_{NN}$ spacing. Thus, we get as a minimum the evidence of anti-clustering of nitrogen atoms as the crystals age. However, taking into account that the N impurity atoms substitute the host P atoms in very perfect diamond-like cubic crystal lattice (it is really perfect according to our data on the position of extremely narrow phonon replica in heavily doped aged GaP:N crystals), we may assert from very simple geometrical consideration that in the case of the equal spacing measured with high accuracy, the N impurity system also forms a cubic crystal superlattice that means not simply anti-clustering, but the ordering of impurities as well as the perfection of the host lattice modified by impurities.

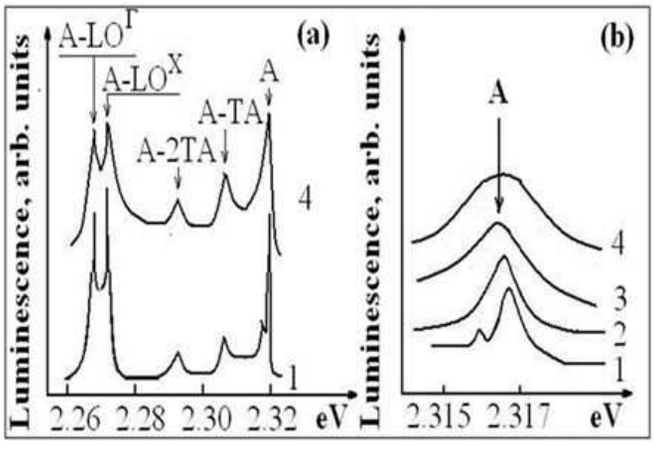


**Figure 8.** Evolution of the GaP:N luminescence with time and nitrogen concentration at a temperature of 15K. **a.** Zero-phonon line of the bound exciton A and its transversal acoustic (TA) and longitudinal optic (LO) phonon replica in as-prepared (4) and 25-year long-term ordered (1) crystals. **b.** Zero-phonon line A as a function of nitrogen (N) concentration. 1-3: 25-year-old crystals. 4: as-prepared. Curves 1 through 4 represent samples with nitrogen concentrations of $10^{17}$, $10^{18}$, $10^{19}$, and $10^{18}$ $cm^{-3}$, respectively.

http://dx.doi.org/10.5772/60431

Figure 8 provides a comparison of the evolution in luminescence spectra at low temperatures (80K and below) from GaP:N over a period of 25 years (original measurement in about 1963). Over this period, zero-phonon line A of single N impurity-bound excitons and their phonon replica are narrower in their line-widths when compared to the freshly prepared single crystals (Figure 8a). Further, as expected, zero phonon line and phonon replica in samples aged at room temperature for 25 years shift spectral position depending upon concentration of N impurities (Figure 8b, spectra 1-3) according to Ref. [40], while the same freshly prepared crystals exhibited broader luminescence line-widths with increasing nitrogen content (Figure 8b, spectrum 4). These, along with other half-centennial findings, including modifications of luminescence kinetics, spontaneous Raman scattering, X-ray diffraction, absorption spectra, micro-hardness, and density of dislocations, which are reported elsewhere [1, 3-24], strongly suggest that close-to-ideal GaP:N crystals are formed over time due to the equally spaced disposition of N impurities from their chaotic distribution in the same freshly prepared crystals.

As first noted in Ref. [23], these results suggest a new type of crystal lattice in which the host atoms occupy their proper (equilibrium) positions in the crystal, while the N impurities, periodically substituted into the lattice, portion it into short chains of equal length. According to the data obtained from Raman light scattering [10, 14], host atoms of this new lattice develop harmonic vibrations, and a high degree of lattice perfection leads to an abrupt decrease in the non-radiative recombination and an increase of efficiency and spectral range of luminescence.

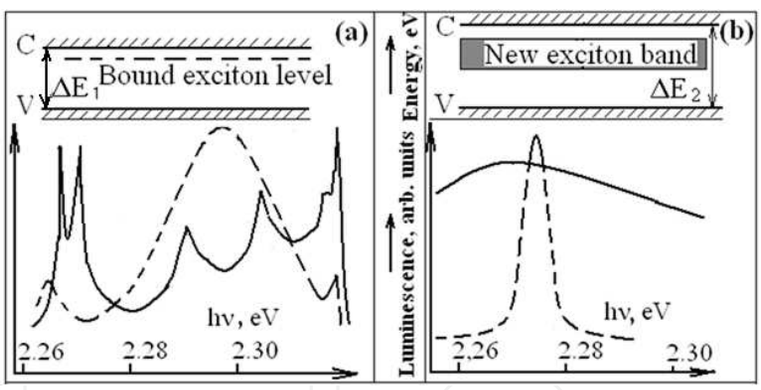


**Figure 9.** Luminescent spectra and schematic representation of the forbidden gaps ($\Delta E_1$, $\Delta E_2$) in the nitrogen-doped GaP aged for (**a**) 25 years and (**b**) 40 years. The dotted lines correspond to highly optically excited crystals. C and V represent the positions of the bottom of the conductance and the top of valence bands, respectively.

Additionally, stimulated emission of light in these temporally ordered crystals (Figure 9b) is observed. As also shown in Ref. [23], the GaP:N crystals aged for at least 40 years possess no discrete impurity level for N-bound excitons in the forbidden gap. They also demonstrated a uniform luminescence from a broad excitonic band instead of the narrow zero-phonon line and its phonon replica as observed from the less-aged 25-year-old crystals.

Thus, long-term ordered GaP:N crystals demonstrate uniform bright luminescence from a broad excitonic band instead of the narrow zero-phonon line and its phonon replica in disordered and partly ordered (25-year-old) crystals. This is due to the fact that ordered crystals have no discrete impurity level in the forbidden gap. To the best of our knowledge, such

transformation of a discrete level within the forbidden gap into an excitonic band (Figure 9 a, b) is observed for the first time. In this case, the impurity atoms regularly occupy the host lattice sites and affect the band structure of the crystals, which is now a dilute solid solution of GaP-GaN with regular disposition of N atoms rather than GaP doped by occasionally located N atoms. Note that the increase of luminescence excitation in case of partly ordered GaP:N (Figure 9a, dotted line) leads to a broad luminescence band as a result of bound exciton interaction [9], while in the case of perfectly ordered crystals (Figure 9b) one can see an abrupt narrowing of the luminescence band, probably due to stimulated emission in defect-free crystals. Earlier, in freshly prepared crystals, we observed a clear stimulated emission from a GaP:N resonator at 80K [5], as well as the so-called superluminescence from GaP single crystals having natural faceting. Presently, our ordered crystals have a bright luminescence at room temperature that implies their perfection and very low light losses. In our studies [14, 23], we demonstrate that the stimulated emission in GaP also developed even at room temperature by direct electron–hole recombination of an electron at the bottom of the conduction band with a hole at the top of the valence band and the LO phonon absorption.

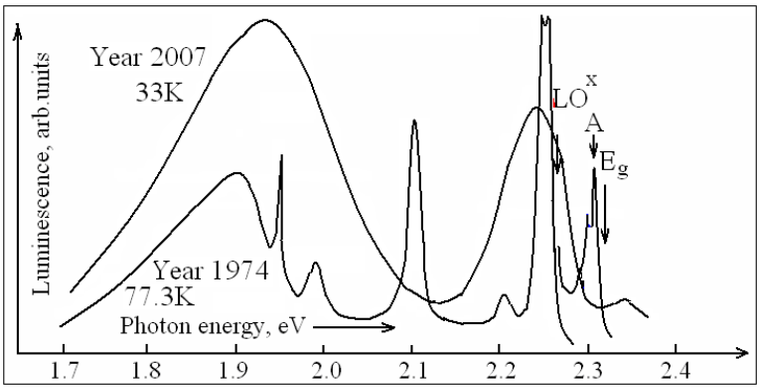


**Figure 10.** Evolution of GaP:N:Sm luminescence between 1973 and 2007. The crystals are grown in 1965.

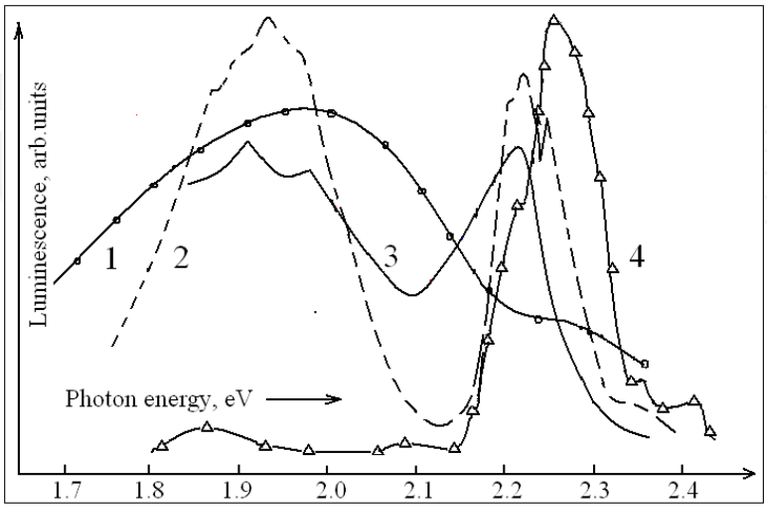


**Figure 11.** Luminescence of long-term ordered GaP:N:Sm. 1, 2—low; 3, 4—room temperatures. 1, 3—low; 2, 4—high excitation.

http://dx.doi.org/10.5772/60431

Investigating earlier luminescence of GaP doped by Sm and Ge, we have demonstrated bright luminescence in infrared region and opportunities to change in the wide wavelength diapason the position of luminescent maximum. For the first time, the GaP:N:Sm crystals were investigated in the year 1974 when their luminescence could be observed only at 80K and below [6]. The relevant spectrum, obtained in the year 1974, is shown in Fig. 10. Then it consisted of two parts: 1) the green part reflecting recombination of N bound excitons through the emission of the narrow zero-phonon A line and its phonon replica, arising in the emission of LO and other lattice phonons, and 2) the red and yellow parts reflecting the absorption of the bound exciton irradiation by Sm centers and its characteristic radiative recombination. In the year 2007 (Fig. 10, [13]), the spectrum of luminescence also consisted of these two parts, but instead of narrow excitonic lines we see a broad green excitonic band and also the broad red and yellow band without any fine structure.

Efficiency of Sm excitation at the N bound exciton recombination highly depends on a degree of uniformity of the N-Sm mixture. The long-term ordering gives a uniform mixture of Sm and N impurities and according to R. L. Bell [43], it provides up to 100% quantum efficiency of radiation from GaP:N:Sm system and bright luminescence at 300K. The bright emission bands at 300K, shown in Figure 11, curves 3, 4, arise as a result of formation during the period 1963–2010 of the uniform mixture of N recombination and Sm activation centers. The luminescence spectra of GaP:N:Sm at low temperatures (35K and below, Figure 11, spectra 1, 2) have the same maxima in green and red and yellow regions where the ratio of their intensities depends on the concentrations of N and Sm impurities as well as on the level of excitation. For instance, at a chosen level of excitation and an N/Sm ratio of concentration one can realize pure red or green emission of high efficiency or any combination of these colors that is an important property of a tunable light source.

Thus, doping GaP simultaneously with Sm and N, choosing necessary temperature and intensity of excitation we can get light emission from green to red. However, further expansion of the emissive spectrum in GaP can be achieved using some of the following other dopants or specific methods of crystal preparation.

Let us now discuss a possibility to converse visible emission into infrared region. Obviously, it is possible, creating in GaP an additional to the basic green another channel for light emissive electron-hole recombination in infrared region. For instance, it is known that the donor-acceptor pair $Ge^A$-$O^D$ on the base of oxygen ($O^D$) and germanium ($Ge^A$) emits the band with the maximum at 1.38 eV [44]. It was shown in Ref. [7] and in some other works fulfilled under the author's supervision, the existence of this band and its intensity, compared with the basic green emission, depends on the concentration of Ge-O pairs and intensity of excitation, obtained with the help of a Q-switched Nd glass laser supplied with the frequency doubler generating 2.34 eV photons.

Increasing the intensity of excitation, one can decrease the contribution into luminescence of light emissive recombination through the Ge-O pairs when the concentration of these pairs will be equal and less than the concentration of electron-hole pairs generated by the laser excitation source. In these conditions will be also clear detected the growing with excitation contribution into the whole light emission from the other recombination channels depressed

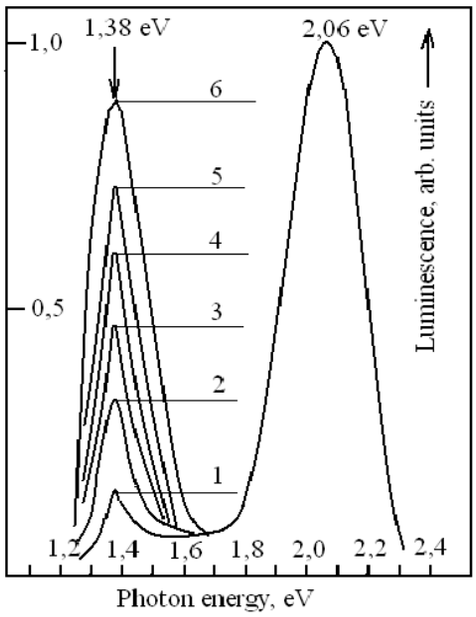


**Figure 12.** Luminescent spectra of GaP doped by Ge with a concentration of approximately $10^{18}cm^{-3}$ at 77.3K and different excitation intensity $I_{ex}$ x $10^{-24}$ $cm^{-2}sec^{-1}$: 16(1); 10(2); 4,5(3); 2,3(4); 1,2(5); and 0,46(6).

by the recombination through Ge-O pairs. Thus, the switching of light emissive recombination channels, important for application in optoelectronic devices, will be observed and demonstrated in the luminescence of GaP doped by Ge. Figure 12 demonstrates depending on excitation intensity the switching of luminescence at 77.3K from infrared with maximum at 1.38 eV to green-yellow region with maximum at 2.06 eV [7].

Moving to infrared region with the help of GaP doped by Ge, we have reached 1.2 eV in the emissive spectrum that 1 eV less than the forbidden gap of GaP crystals. Taking into account that our goal is to propose a cheap, resource-saving, and impactful way for the development of optoelectronics with the help of the special transformation of an ordinary semiconductor into the base material for various light emissive devices structures with broad and bright light emissive spectra, let us consider opportunities to expand light emission as much as possible to the ultraviolet (UV) region, using only GaP bulk and nanocrystals instead of a lot of the other semiconductors with their complicated, labor-consuming, and expensive technologies of preparation of materials with necessary reliable radiative properties.

As we have shown previously [8-17], different defects of high concentration in freshly prepared GaP single crystals completely suppress any luminescence at room temperature due to negligible small free path for non-equilibrium electrons and holes between the defects with their non-radiative recombination, while the quantum theory predicts free movement of electrons and holes in the field of an ideal crystal lattice. It was also shown that the long-term ordered and therefore close-to-ideal crystals demonstrate bright luminescence and stimulated emission repeating behavior of the best nanoparticles with pronounced quantum confinement effects. Therefore, there are only two ways of preparing a material with bright luminescence from IR to UV regions: to prepare very perfect, defectless single crystals or nanocrystals with

http://dx.doi.org/10.5772/60431

the dimensions less than electron-hole free path in this material of standard quality. Correctness of the chosen way can be confirmed by the following comparison of optical properties of the best GaP nanocrystals and GaP perfect bulk single crystals.

## 5. Comparison of Optical Properties of GaP Nanocrystals and GaP Perfect Bulk Single Crystals

Jointly with the references [3, 7, 9-17, 21-27, 32] here we present a generalization of the results on long-term observation of luminescence, absorption, and Raman light scattering in bulk semiconductors in comparison with some properties of the best to the moment GaP nanocrystals. The combination of these characterization techniques elucidates the evolution of these crystals over the course of many years, the ordered state brought about by prolonged room-temperature thermal annealing, and the interesting optical properties that accompany such ordering. We demonstrate that long-term natural stimuli improve the perfection of our crystals, which can lead to novel heterogeneous systems and new semiconductor devices with high temporal stability. Raman light scattering confirms high quality of the long-term ordered crystals.

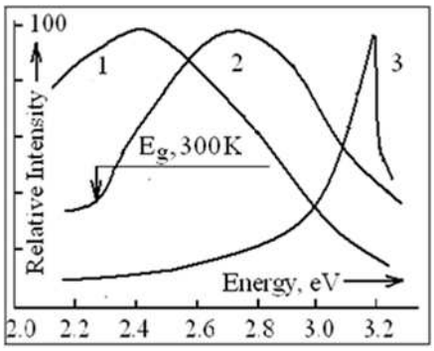


**Figure 13.** Luminescence of perfect bulk GaP single crystals (1) in comparison with the luminescence of GaP nanoparticles and GaP/polymers nanocomposites (2, 3). Nanoparticles were prepared from white P by mild aqueous or colloidal synthesis at decreased temperature, stored as the dry powder (spectrum 2) or suspension in a liquid (spectrum 3). Details: [15, 17].

We further improved upon the preparation of GaP nanocrystals using the known methods of hydrothermal and colloidal synthesis [30-32] by taking into account that the success of our activity depends on the optimal choice of the types of chemical reactions, necessary chemicals and their purity, conditions of the synthesis (control accuracy, temperature, pressure, duration, etc.), methods and quality of purification of the nanocrystals, and storage conditions for nanoparticles used in the further operations of fabrication of the GaP nanocomposites. The best quality GaP nanoparticles have been prepared by hydrothermal or colloidal synthesis from white phosphorus at decreased temperature (125°C) and intense ultrasonication; it was established that the maximum shift of their luminescence to ultraviolet and the best quality in general have the nanocomposites obtained from the nanoparticles of the same dimensions stored as a suspension in a suitable liquid.

Figure 13 compares the luminescence spectra of our long-term (up to 50 years) ordered GaP single crystals (spectrum 1) to that from high quality GaP nanoparticles and their GaP nanoparticles/polymers nanocomposites [15, 17]. Nanocrystals of the different dimensions, stored as dry powder, demonstrate rather broad luminescent band with maximum at 2.8 eV (Figure 13, spectrum 2), while the nanocrystals of about 10 nm sizes, thoroughly separated and distributed in a suspension, that prevent their coagulation, mechanical, and optical interaction, exhibit bright narrow-band luminescence with a maximum at 3.2 eV, approximately 1 eV above the position of the absorption edge in GaP at 300K (Figure 13, spectrum 3). The thoroughly washed, ultrasonicated and dried nanopowders as well as their specially prepared suspensions have been used for fabrication of blue light emissive GaP nanocomposites on the base of some optically and mechanically compatible with GaP polymers [15, 17, 30-32]. According to our measurements, the matrix polymers PGMA-co-POEGMA or BPVE used in this work provide no contribution to the spectra of luminescence of the based on these matrixes, so, the nanocomposite spectra coincide with those obtained from the relevant GaP powders or suspensions. We note that in the GaP/BPVE nanocomposite, the position of the luminescent maximum can be changed between 2.5 and 3.2 eV and the brightness is 20–30 more than in the PGMA and PGMA-co-POEGMA matrixes.

Long-term ordering leads to the creation of perfect bulk GaP crystals with considerably expanded and bright emissive band, practically the same as in the perfect GaP nanoparticles. We explain the broadening of the luminescence band and the shift of its maximum to low photon energies in luminescence of the nanocomposite based on the GaP powder by presence in the powder of the nanoparticles with the different dimensions between 10 and 100 nm. Meanwhile, the nanocomposites on the base of the suspensions containing only approximately 10 nm nanoparticles exhibit bright luminescence with a maximum at 3.2 eV due to a high transparency of 10 nm nanoparticles for these high energy emitted photons and pronounced quantum confinement effect.

In accord with our data [15, 31] the shift due to the quantum confinement effects is about a few tenths of eV and, obviously, it is impossible to explain only through this effect the dramatic 1 eV expansion of the region of luminescence at 300K to the high-energy side of the spectrum. In order to explain this interesting phenomenon, we postulate that the nanocrystals, much like the ideal long-term ordered bulk GaP single crystals, where this effect is not so strong, exhibit the huge increase in blue-shifted luminescence due to: (a) negligibly small influence of defects and non-radiative recombination of electron-hole pairs and very high efficiency of their radiative annihilation, (b) high perfection of nanocrystal lattice, and (c) high transparency of nanocrystals due to their small dimensions for the light emitted from high points of the GaP Brillouin zones, for instance, in the direct transitions $\Gamma_1^c$–$\Gamma_{15}^v$ between the conductive and valence bands with the photon energy at 300K equal to 2.8 eV [37], and (d) high efficiency of this so-called "hot" luminescence that means direct radiative recombination of electrons without their preliminary thermalization into the nearest particular point of the conductance band. Taking into account the high light absorption coefficient equal to approximately $10^5$ $cm^{-1}$ for photons with the energy in the vicinity of maximum at 3.2 eV [38], we can explain the difference in the spectrum 1 from perfect bulk GaP crystal and the spectrum 3 from its 10 nm perfect nanoparticles. Really, a big GaP single crystal, even very perfect one, in principle, cannot emit many photons in UV region, because the overwhelming majority of those photons

will be immediately absorbed in the crystal; only tiny defectless 10 nm GaP spheres, transparent for this UV region, distributed in the transparent suspension or a polymer film will easily emit this UV light.

Note, our first attempts to prepare GaP nanoparticles [18, 28] yielded room temperature luminescence with the maximum shifted only to 2.4 eV in comparison with the achieved now new maximum at 3.2 eV and it confirms our significant progress in preparation of GaP nanoparticles and GaP/polymers nanocomposites. The perfect quality of the nanoparticles prepared by improved technologies is confirmed by all the used methods of characterization, while investigation of Raman light scattering evolution during 25 years (since 1989) clear confirms considerable improvement of GaP single crystal quality and the existence of new interesting phenomena characterizing only very perfect crystals.

On the base of these improved technologies for the preparation of GaP nanoparticles and GaP/polymer nanocomposites, we can change within the broad limits the main parameters of luminescence and create a framework for novel light emissive device structures using dramatic 1 eV expansion of GaP luminescence to UV region. Besides that, using all the noted in the presented review opportunities, including specially doped GaP and the necessary level of luminescence excitation, we can change the position of maximum and bandwidth of luminescence in wide, from infrared 1.2 to UV 3.2 eV, limits.

## 6. Excitonic Crystal and Its Importance in Optoelectronics

The role and application of bound excitons in nanoscience and technology are discussed in this chapter. Bound excitons are well studied in semiconductors, especially in gallium phosphide doped by nitrogen (GaP:N) [3, 4, 7, 38, 40, 45]. Doping of GaP with N leads to isoelectronic substitution of the host P atoms by N in its crystal lattice and to the creation of the electron trap with a giant capture cross-section. Therefore, any non-equilibrium electron in the vicinity of the trap will be captured by N atom, attracting a non-equilibrium hole by Coulomb interaction and creating the bound exciton — short-lived nanoparticle with the dimension of the order of 10 nm (it is the Bohr diameter of bound exciton in GaP:N). Note, that none of nanotechnology methods are used in the creation or selection of dimensions of these nanoparticles — only natural forces of electron–hole interaction and electron capture by the traps are necessary for the creation of these nanoparticles. As the result we get something like neutral short-lived atom analogue — a particle consisting of heavy negatively charged nucleus (N atom with captured electron) and a hole. So-called zero vibrations do not destroy the possible solid phase of bound excitons having these heavy nuclei that give an opportunity to reach in GaP:N a new crystal state — the short-lived excitonic crystal appeared at the necessary level of excitation, N impurity ordering and concentration, energy of photons and temperature.

Taking into account the above-mentioned preceding results, a model for the GaP:N long-term ordered crystal and its behavior at the relevant level of optical excitation for 40-year-old ordered N-doped GaP (Figure 14) can be suggested. At the relevant concentrations of N, the anion sub-lattice can be represented as a row of anions where N substitutes for P atoms with

the period equal to the Bohr diameter of the bound exciton in GaP (approximately 10 nm) (Figure 14a). At some level of optical excitation, all the N sites will be filled by excitons, thereby creating an excitonic crystal (Figure 14b), which is a new phenomenon in solid-state physics and a very interesting medium for application in optoelectronics and nonlinear optics [4, 15, 17, 25, 26].

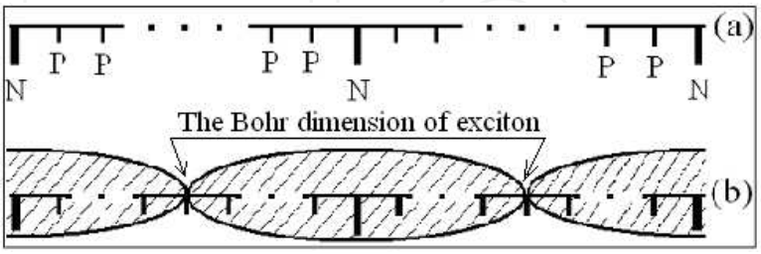


**Figure 14.** The models of 40 years ordered GaP doped by N. **a.** The new type of crystal lattice with periodic substitution of N atoms for the host P atoms. **b.** The excitonic crystal on the base of this lattice. The substitution period is equal to the Bohr diameter of exciton (~ 100Å) and optical excitation is enough for complete saturation of the N sublattice (please see details in Refs. [15, 17]).

Thus, using bound excitons as short-lived analogues of atoms and sticking to some specific rules, including the necessity to build in the GaP:N single crystal the excitonic superlattice with the identity period equal to the bound exciton Bohr dimension, we get a unique opportunity to create a new solid state media — consisting from short-lived nanoparticles excitonic crystal, obviously, with very useful and interesting properties for the application in optoelectronics, nanoscience, and technology. The following will discuss methods of preparation and possible application in optoelectronics of perfect GaP crystals, based on perfect GaP excitonic crystals and nanocrystals.

## 7. Already Discovered and Possible Nonlinear Optical Phenomena in GaP

Thus, confirmed by this semicentennial study, the impurities in doped long-term ordered GaP create a sublattice with a period that depends on their concentration. By periodically substituting for host atoms or occupying interstitial sites in the host lattice, the impurities become an intrinsic component of the modified crystal lattice and participate in the formation of a "new" phonon spectrum.

The ordered crystals with the host lattice modified by impurities could be very useful in various optoelectronic applications. Noted here are only a few potential applications in light emissive device structures. The properties of these structures will be very stable and independent on time. Uniform distribution of the recombination (N) and activator centers at the optimum concentration will yield the maximum efficiency for light emission. Further investigations of the quasi-crystalline state of excitons (or bi-excitons) bound to an impurity superlattice with a period equal to the Bohr dimension will be very interesting and useful because they should greatly strengthen nonlinear optical effects at low excitation intensities. This excitonic phase

http://dx.doi.org/10.5772/60431

of high density of photons as an original accumulator of light also provides new opportunities for storage, transmission, and conversion of light.

With significant recent progress in semiconductor thin film deposition and growth techniques in some specific cases of device optoelectronic structure preparation, there obviously will be no longer a need to wait during years for such ordering to occur. For instance, superlattice from GaP/GaP:N with the period of the order of the bound excitons (their Bohr radius is equal to 5 nm) can be prepared by molecular beam epitaxy (MBE) or by MBE in combination with the laser-assisted epitaxy (LAE) [46-48]. Further, the preparation of a two- or three-dimensional arrangement of N impurities in a GaP film is difficult but also possible with the help of ion lithography. Of course, nowadays this technique is a frontier of our technological possibilities, but within the nearest future some very important progress likely will be obtained also in this direction. In this case, we will get a unique opportunity to design 3-dimensional impurity superlattices with configuration, symmetry, and lattice that are optimal for application in a concrete device structure or for efficient realization of specific linear or nonlinear optical phenomena. In any case, independently on the method of creation, the impurity modified crystal lattices, the excitonic (as well as bi-excitonic) phase with translational symmetry are very interesting objects, the properties and possible application of which are now under our investigation.

Nonlinear optics, starting its epoch-making development from the Nobel Prize Laureate N. Bloembergen transaction [49], with the appearance of lasers and highly supported personally by one of their inventors, the Nobel Prize Laureate A. Prokhorov, who helped the author to found in 1985 the Laser Research Laboratory in the Academy of Sciences of Moldova, since 1960s has taken its noteworthy place in investigations of GaP [5, 7, 50-52]. Here especially important for fundamentals and application in optoelectronic device structures were investigations of direct and indirect (with participation of the lattice phonons) many-quantum absorption between high symmetry points of GaP Brillouin zone (Figure 1), following the increase of photoconductivity and UV photon emission. So, exciting these high symmetry points with the help of infrared photon of a Q-switched laser, we get photoconductivity with participation of different energy bands and UV photon emission that is important equally for the investigation of band structure and for application in light frequency convertors. Addition of new opportunities due to elaboration of defectless perfect GaP bulk single crystals, its top-quality nanoparticles and multi-layered structures, discovery of the new nonlinear optic medium – excitonic crystal and its very interesting nonlinear optical phenomena [25-27] will surge of interest to this crystal, giving a new prospective industrial method of perfect crystal preparation, as well as opportunities for efficient realization in optoelectronics and electronics in general of remarkable properties of semiconductors due to a big commercial advantage from their fabrication.

## 8. Conclusions

Since the time of original preparation of gallium phosphide doped by nitrogen crystals (GaP:N) by the author in the 1960s, followed by the introduction of the excitonic crystal concept in the 1970s, the best methods of bulk, film, and nanoparticle crystal growth were elaborated. The

results of semi-centennial evolution of GaP:N properties are compiled here and in the references to this paper. Novel and useful properties of GaP including an expected similarity in behavior between nanoparticles and perfect bulk crystals, as well as very bright and broadband luminescence at room temperature, are observed. These results provide a new approach to the selection and preparation of perfect materials for optoelectronics [25] and a unique opportunity to realize a new form of solid-state host — the excitonic crystal [26, 27]. In spite of the fact that the time necessary for natural long-term ordering (years) does not lead to optimism, the collected experience and results confirm expedience of the efforts directed to the formation in GaP of the N impurity superlattice having the identity period equal to the bound exciton dimension. As noted in Ref. [25], the process of preparation of top quality material for industrial electronics can be organized if the freshly grown crystals will be kept for years in a special storage and only old crystals (like to the old wine, if to use close to Moldova and other winemaking countries analogy) with the necessary properties will be annually retrieved for device fabrication while new portions of fresh crystals will be placed for long-term ordering.

Except natural aging of the relevant crystals for years, preparation of the N superlattice for excitonic crystal can be also realized by known methods of growth of multi-layer films, in particular by molecular beam and laser-assisted epitaxy [46-48].

The excitonic crystal, created by the long-term ordering or by the noted above methods of growth of multi-layer films, as well as the bulk top quality GaP crystals with the unique optic properties, obtained by the long-term ordering process of freshly prepared crystals, will be used in the new generation of optoelectronic devices, sometimes instead of nanoparticles and a lot of other materials. In particular, keeping in mind the low energy of the bound exciton creation, one can expect a low threshold for the generation of non-linear optical effects in the excitonic crystal and a good opportunity to create new and very efficient optoelectronic devices.

Note that semiconductor nanoparticles were introduced into materials science and engineering mainly in order to avoid limitations inherent to freshly grown semiconductors with a lot of different defects. However, it was shown [15] that this reason becomes unessential if, when justified, perfect long-term ordered semiconductor crystals are applied in electronics. Independently on their dimensions they demonstrate very interesting for application properties. Therefore, using the long-term ordered, perfect GaP crystals or similar on behavior and properties material in the electronic industry instead of the elaboration of very expensive and labor-consuming technologies for diverse materials and their nanoparticles with limited for application spectral region and other parameters, we get a big commercial advantage from their fabrication and application (for details please see the paper [25]).

All the obtained results presented here and included in summary reviews [15, 17, 25-27] may sufficiently change the approach to the selection of materials necessary for electronics, to make cheaper and simpler technology for the preparation of the selected materials and device structures based on them. This study of long-term convergence of bulk- and nanocrystal properties brings a novel perspective to improving the quality of semiconductor crystals. The unique collection of pure and doped crystals of semiconductors grown in the 1960s provides

http://dx.doi.org/10.5772/60431

an opportunity to observe the long-term evolution of properties of these key electronic materials. During this half-centennial systematic investigation we have established the main trends of the evolution of their optoelectronic and mechanical properties. It was shown that these stimuli to improve the quality of the crystal lattice are the consequence of thermodynamic driving forces and prevail over tendencies that would favor disorder and destruction. Our long-term ordered and therefore close to ideal crystals repeat the behavior of the best nanoparticles with pronounced quantum confinement effect.

For the first time, to the best of our knowledge, we have observed a new type of the crystal lattice where the host atoms occupy their proper (equilibrium) positions in the crystal field, while the impurities, once periodically inserted into the lattice, divide it in the short chains of equal length, where the host atoms develop harmonic vibrations. This periodic substitution of a host atom by an impurity allows the impurity to participate in the formation of the crystal's energy bands. In GaP it leads to the change in the value of the forbidden energy gap, to the appearance of a crystalline excitonic phase, and to the broad excitonic energy bands instead of the energy levels of bound excitons. The high perfection of this new lattice sharply decreases non-radiative electron-hole recombination, increases efficiency and the spectral range of luminescence, and promotes the stimulated emission of light due to its amplification inside the well-arranged, defect-free crystal. The development of techniques for the growth of thin films and bulk crystals with ordered distribution of impurities and the proper localization of host atoms inside the lattice are our high priority.

Semiconductor nanoparticles were introduced into materials science and engineering mainly to avoid limitations inherent to freshly grown semiconductors with a lot of different defects. Here and in other publications we show that this reason becomes unessential if we will apply in electronics, when it is justified, perfect long-term ordered semiconductors, which demonstrate independently on their dimensions very interesting for application properties. Especially important for application in the new generation of light emissive devices are the predicted and investigated by us crystalline state of bound excitons in GaP:N, the discovered in the framework of the STCU Project 4610 [16, 32] dramatic expansion of luminescence region in GaP perfect bulk single crystals as well as in the best prepared GaP nanocrystals and based on them composites with transparent polymers.

Using the long-term ordered GaP or similar on behavior and properties material in the electronic industry instead of elaboration of very expensive and labor-consuming technologies for diverse materials with their limited for application spectral region and other parameters, we get a big commercial advantage from their fabrication and application. So, the results of this long-term evolution of the important properties of our unique collection of semiconductor single crystals promise a novel approach to the development of a new generation of optoelectronic devices.

Besides the long-term ordering, the combined methods of laser-assisted and molecular beam epitaxies [46-48] will be applied to fabrication of device structures with artificial periodicity; together with classic methods of the perfect crystal growth, they can be employed to realize impurity ordering that would yield new types of nanostructures and enhanced optoelectronic device performance.

For the first time we demonstrate that well-aged GaP bulk crystals as well as high quality GaP nanoparticles have no essential difference in their luminescence behavior, brightness, or spectral position of the emitted light. The long-term ordered and therefore close to ideal crystals repeat the behavior of the best nanoparticles with pronounced quantum confinement effect. These perfect crystals are useful for application in top-quality optoelectronic devices and are a new object for the development of fundamentals of solid state physics.

Of course, waiting for improvement of the crystal quality for tens of years can be justified only in exceptional cases, but we propose to turn this perennial procedure of long-term ordering into the necessary one for the preparation of the top quality material for industrial electronics, which due to its unique properties will be used in electronic devices instead of a lot of various materials.

## Acknowledgements

I am glad to note that the broad discussion and dissemination of our joint results stimulate the development of our further collaboration with reliable partners from the USA, Russia, Italy, Romania, France, and other countries. I express my cordial gratitude to my teachers, the late world-known scientists: Professor Nina A. Goryunova, Nobel Prize Laureate Alexander M. Prokhorov, Professors Rem V. Khokhlov, and Sergei I. Radautsan. The author is very grateful to the US Department of State, the Institute of International Exchange, Washington, DC, the US Air Force Office for Scientific Research, the US Office of Naval Research Global, Civilian R&D Foundation, Arlington, VA, Science & Technology Center in Ukraine, to his colleagues and co-authors from Clemson University, SC, University of Central Florida, FL, Istituto di elettronica dello stato solido, CNR, Rome, Italy, Universita degli studi, Cagliari, Italy, Lomonosov Moscow State University, Ioffe Physico-Technical Institute and State Polytechnical University, St. Petersburg, Prokhorov General Physics Institute of the Russian Academy of Sciences, Moscow, Russia, the Institute of Applied Physics of the Academy of Sciences of Moldova for support and attention to this protracted (1963–present time) research.

## Author details

Sergei L. Pyshkin[1,2]

Address all correspondence to: spyshki@clemson.edu

1 Academy of Sciences of Moldova, Republic of Moldova

2 Clemson University, USA

## References

[1] Goryunova NA, Pyshkin SL, Borshchevskii AS, et al. Influence of impurities and crystallisation conditions on growth of platelet GaP crystals. Symposium on Crystal Growth at the 7th Int Crystallography Congress (Moscow, July 1966). J Growth Crystals 1969; 8 68-72, ed. N.N. Sheftal, New York.

[2] Pyshkin SL, Radautsan SI, Zenchenko VP. Processes of long-lasting ordering in crystals with a partly inverse spinel structure. J Soviet Phys – Doklady 1990; 35(4) 301-4.

[3] Pyshkin SL. Preparation and properties of gallium phosphide. Ph.D. thesis 1967, State University of Moldova, Kishinev.

[4] Pyshkin SL, Zifudin L. Excitons in highly optically excited gallium phosphide. J Luminescence 1974; 9 302-8.

[5] Pyshkin SL (presented by Nobel Prize Laureate A.M. Prokhorov). Stimulated emission in gallium phosphide. J Soviet Physics – Doklady 1975; 19 845-6.

[6] Pyshkin S. Luminescence of GaP:N:Sm crystals. J Soviet Phys Semicond 1975; 8: 912-3.

[7] Pyshkin SL. Photoconductivity and luminescence of highly optically excited semiconductors. Dr.Sc. thesis 1978, Lomonosov Moscow State University.

[8] Pyshkin S, Anedda A, Congiu F, Mura A. Luminescence of the GaP:N ordered system. J Pure Appl Optics 1993; 2 499-502.

[9] Pyshkin S, Anedda A. Time-Dependent Behaviour of Antistructural Defects and Impurities in Cd-In-S and GaP. Institute of Physics Conference Series 1998, Ternary and Multinary Compounds; 152, Section E 785-9.

[10] Pyshkin S, Ballato J, Chumanov G. Raman light scattering from long-term ordered GaP single crystals. J Optics 2007, J Opt A Pure and Appl Optics; 9 33-6.

[11] Pyshkin SL, Ballato J, Bass M, Turri G. Luminescence of Long-Term Ordered Pure and Doped Gallium Phosphide. TMS Annual Meeting, invited talk at the Symposium: Advances in Semiconductor, Electro Optic and Radio Frequency Materials, March 9–13, New Orleans, LA. J Electron Mater 2008; 37(4) 388-95.

[12] Pyshkin SL, Ballato J, Bass M, Chumanov G. Time-dependent evolution of crystal lattice, defects and impurities in CdIn2S4 and GaP. J Phys Status Sol 2009; C(6) 1112-5.

[13] Pyshkin SL, Ballato J, Bass M, Turri G. Evolution of luminescence from doped gallium phosphide over 40 Years. J Electron Mater 2009; 38(5) 640-6.

[14] Pyshkin S, Ballato J. Evolution of optical and mechanical properties of semiconductors over 40 Years. J Electron Mater 2010; 39(6) 635-41.

[15] Pyshkin SL, Ballato J. Long-term convergence of bulk- and nano-crystal properties. In: Predeep P (ed.) Optoelectronics – Materials and Techniques 2011. Rijeka: InTech; 459-76.

[16] Pyshkin S, Ballato J. Dramatic expansion of luminescence region in GaP/polymer nanocomposites: Supplemental Proceedings, vol.1: "Materials Processing and Interfaces": 353-9, TMS Annual Meetings, Orlando, FL, USA, March 11-15, 2012.

[17] Pyshkin SL, Ballato J. Advanced light emissive device structures. In: Pyshkin SL and Ballato J (ed.) Optoelectronics – Advanced Materials and Devices 2013. Rijeka: InTech; 1-24.

[18] Pyshkin S, Ballato J, Chumanov G, DiMaio J, Saha AK. Preparation and Characterization of Nanocrystalline GaP: Technical Proceedings of the 2006 NSTI Nanotech Conference; 3 194-7.

[19] Pyshkin SL, Ballato J, Chumanov G. Optical Characterization of Long -Term Ordered and Nanocrystalline GaP, (invited), 3rd Int. Conf. on Materials Science and Condensed Matter Physics (Kishinev, Moldova, Oct 2006), Abstract Book, p172; Mold. J. of the Physical Sciences 2007; 6(2) 148-159.

[20] Pyshkin SL, Ballato J, Belevschii S, Rusu E, Racu A, Van DerVeer D. Synthesis and Characterization of GaP Nanoparticles for Light Emissive Devices: The 2011 NSTI-Nanotech Conference Proceedings: www.nsti.org, ISBN 978-1 4398-7142-3 1, 327-30, Boston, MA, June 13-16.

[21] Pyshkin SL, Ballato J, Bass M, Chumanov G, Turri G. Time-dependent evolution of crystal lattice, defects and impurities in $CdIn_2S_4$ and GaP. Phys Stat Sol 2009; C(6) 1112-5.

[22] Pyshkin S, Zhitaru R, Ballato J, Chumanov G, Bass M. Structural Characterization of Long-Term Ordered Semiconductors: The 2009 MS&T Conference Proceedings, International Symposium ''Fundamentals & Characterization'' 698-709, Pittsburgh, October 24-29.

[23] Pyshkin S, Ballato J, Bass M, Chumanov G, Turri G. Properties of the long-term ordered semiconductors: The 2009 TMS Annual Meeting and Exhibition Suppl. Proceedings; 3 477-84, San Francisco, February 15–19.

[24] Pyshkin S, Ballato J, Chumanov G, Bass M, Turri G, Zhitaru R, et al. Optical and Mechanical Properties of Long-Term Ordered Semiconductors. Moldavian J Phys Sci 2009; 8(3-4) 287-95. The 4th Int Conference on Materials Science and Condensed Matter Physics, Kishinev, Sept 23-26, 2008.

[25] Pyshkin SL. Gallium Phosphide - New Prospect for Optoelectronics. J Adv Optoelectron Mater 2013 (ISSN Online: 2327-7661, ISSN Print: 2327-767X); 1(4) 59-66.

[26] Pyshkin SL. Excitonic crystal and nanotechnology. Symbiosis J Nanosci Technol: Open Access 2014; 1(2), http://symbiosisonlinepublishing.com/nanoscience-technology08.pdf.

[27] Pyshkin SL. Excitonic Crystal, Nanotechnology and New Prospect for Optoelectronics, J Open Optics 2015; 9 26-37.

[28] Pyshkin S, Ballato J. Advanced Light Emissive Composite Materials for Integrated Optics: The 2005 MS&T Conference Proceedings, Symposium: The Physics and Materials Challenges for Integrated Optics - A Step in the Future for Photonic Devices 3-13, Pittsburgh, PA.

[29] Pyshkin S, Ballato J, Luzinov I, Zdyrko B. Fabrication and Characterization of the GaP/Polymer Nanocomposites for Advanced Light Emissive Device Structures: The 2010 NSTI-Nanotech Conference Proceedings; 1 772-5. www.nsti.org, ISBN 978-1-4398-3401-5, Anaheim, CA, Jun 21-24, 2010.

[30] Pyshkin S, Ballato J, Chumanov G, Tsyntsaru N, Rusu E. Preparation and Characterization of Nanocrystalline GaP for Advanced Light Emissive Device Structures: The 2010 NSTI-Nanotech Conference Proceedings; 1 522-5, www.nsti.org, ISBN 978-1-4398-3401-5.

[31] Pyshkin SL, Ballato J, Luzinov I, Zdyrko B. Fabrication and characterization of GaP/polymer nanocomposites for advanced light emissive device structures. J Nanoparticle Res 2011; 13 5565-70, ISSN: 1388-0764, doi: 10.1007/s11051-011-0547-0.

[32] Pyshkin Sergei L (Project Manager). Advanced Light Emissive Device Structures. STCU (www.stcu.int) Project 4610, 2009-2012.

[33] Shanmin Gao, et al. Aqueous synthesis of III-V semiconductor GaP and InP exhibiting pronounced quantum confinement. Chem Commun 2002 3064-5.

[34] Zhengang Liu, Yujun Bai, Deliang Cui, Qilong Wang. Preliminary Insight into the formation process of InP and GaP nanocrystals. Solid State Sci 2003; 5 1037-40.

[35] Zhao-Chun Zhang, Bao-Ping Wang. Diamond and oxidized disordered graphite on the surface of gallium phosphide nanoparticles. Syst Charact 2009; 26 53–7.

[36] Paul W. Band structure of the intermetallic semiconductors from pressure experiments. J Appl Phys 1961; 32 2082-94.

[37] Zallen R, Paul W. Band structure of gallium phosphide from optical experiments at high pressure. Phys Rev 1964; 134 A1628-41.

[38] Dean PJ, Thomas DG. Intrinsic absorption-edge spectrum of gallium phosphide. Phys Rev 1966; 150(2) 690-702.

[39] Kleinman DA, Spitzer WG. Infrared lattice absorption of GaP. Phys Rev 1960; 118 (1) 110-7.

[40] Allen WJ. Energy levels of nitrogen-nitrogen pairs in gallium phosphide. J Phys C 1968, 1 1136-8.

[41] Bairamov B, Kitaev Y, Negoduiko V, Khashkhozhev Z. Light scattering by optical phonons and non-linear optical properties of GaP. J Soviet Phys Solid State 1975; 16 1323-7.

[42] Pyshkin S, Radautsan S, Zenchenko V. Raman spectra of Cd-In-S with different cation-sublattice ordering. J Soviet Phys Doklady 1990; 35(12) 1064-67.

[43] Bell RL. A proposal for a DC pumped rare-earth laser. J Appl Phys 1963; 34 1563-4.

[44] Gershenzon M, et al. Evidence for radiative recombination between deep donor-acceptor pairs in GaP at room temperature. J Appl Phys 1966; 37(2) 483-6.

[45] Thomas DG, Hopfield JJ, Frosch CJ. Isoelectronic traps due to nitrogen in gallium phosphide. Phys Rev Lett 1965; 15 857-9.

[46] Pyshkin SL, et al. Preparation and structural properties of some III-V semiconductor films grown on (100) oriented Si substrates. J Appl Surf Sci 1992; 56-58 39-43.

[47] Budyanu VA, Chechuy SN, Pyshkin SL, et al. Investigation of III-V/Si heterojunction grown by laser deposition. Phys Stat Sol (a) 1985; 91 737-44.

[48] Budyanu VA, Chechuy SN, Pyshkin SL, et al. Laser vacuum epitaxy of III-V semiconductors on silicon. Rev Roumaine de Physique 1987; 32(1-2) 216-9.

[49] Bloembergen N. Nonlinear Optics. Edition: 4th. Paperback – June, 1996.

[50] Ashkinadze BM, Pyshkin SL, Radautsan SI. Some Non-linear Optical Effects in GaP: The IX Int. Conf. on the Physics of Semiconductors Proceedings; 2 1189-93, Moscow, July 1968.

[51] Pyshkin SL, et al. Multi-quantum absorption in GaP. Opto-electronics 1970; 2 245-9.

[52] Ashkinadze BM, Kretsu IP, Pyshkin SL, et al. Luminescence of Gallium phosphide near an indirect transition in the multiphoton excitation case. Soviet Phys Semicond 1969; 2(10) 1261-3.